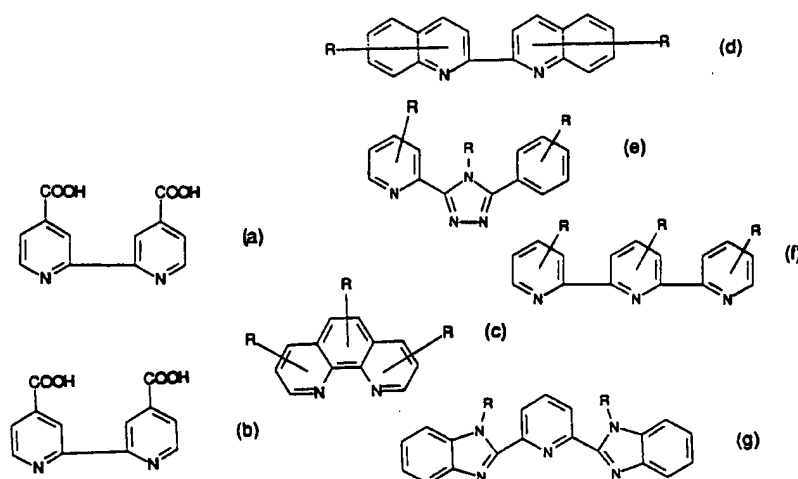




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(21) International Application Number: PCT/EP93/02221 (22) International Filing Date: 19 August 1993 (19.08.93) (30) Priority data: 9217811.0 21 August 1992 (21.08.92) GB (71) Applicant (for all designated States except US): ECOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE (EPFL) [CH/CH]; Ecublens, CH-1015 Lausanne (CH). (72) Inventors; and (75) Inventors/Applicants (for US only) : GRAETZEL, Michael [DE/CH]; Chemin du Marquisat 7a, CH-1015 St-Sul- pice (CH). NAZEERUDDIN, Mohammad, Khaja [IN/ CH]; Avenue du Tir Fédéral 81, CH-1022 Chavannes (CH).		(74) Agent: GANGUILLET, Cyril; Abrema Agence Brevets et Marques, Ganguillet & Humphrey, Rue Centrale 5, Case Postale 2065, CH-1002 Lausanne (CH). (81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>

(54) Title: ORGANIC COMPOUNDS**(57) Abstract**

A compound of formula (I): $(X)_n RuLL_1$ where n is 1 or 2, preferably 2, and in which Ru is ruthenium; each X independently is selected from Cl , SCN , H_2O , Br , I , CN and $SeCN$ and L is a ligand of formulae (a) to (g) and L_1 is selected from a ligand of formulae (a) to (c) where each R independently is selected from OH , hydrogen, $C_{1-20}alkyl$, $-OR_a$ or $-N(R_a)_2$ and each R_a independently is hydrogen or $C_{1-4}alkyl$.

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ORGANIC COMPOUNDS

The invention relates to new transition metal dyestuffs and to their use in photovoltaic cells. These dyes can be coated on titanium dioxide films rendering the device effective in the conversion of visible light to electric energy.

Titanium dioxide films (layers) are known for their semiconductive properties and this property renders them useful for photovoltaic cells. However titanium dioxide has a large band gap and therefore it does not absorb light in the visible region of the spectrum. For solar applications it is important that the titanium dioxide film be coated with a photosensitizer which harvests light in the wavelength domain where the sun emits light, i.e. between 300 and 2000 nm. Thermodynamic considerations show that conversion of solar energy into electricity is achieved in the most efficient fashion when all the emitted photons with wavelengths below 820 nm are absorbed by the photosensitizer. The optimal dye for solar conversion should therefore have an absorption onset around 800nm and the absorption spectrum should be such that it covers the whole visible domain.

A second requirement for efficient solar light energy conversion is that the dyestuff after having absorbed light and thereby acquired an energy-rich state is able to inject with practically unit quantum yield, an electron in the conduction band of the titanium dioxide film. This requires that the dyestuff is attached to the surface of the titanium dioxide through suitable interlocking groups. The function of the interlocking group is to provide electronic coupling between the chromophoric group of the dyestuff and the conduction band of the semiconductor. This type of electronic coupling is required to facilitate electron transfer between the excited state of the dyestuff band the conduction band. Suitable interlocking groups are p-conducting substituents such as carboxylate groups, cyano groups, phosphate groups or chelating groups with p-conducting character such as oximes, dioximes, hydroxy quinolines, salicylates and

alpha keto enolates. The electrons, photoinjected by the dyestuff, generate electrical current in the external circuit when the photovoltaic cell is operated.

Accordingly a new series of dyes has been developed to act as a photosensitizer.

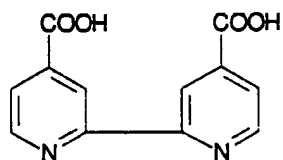
According to the invention, there is provided a compound of formula I



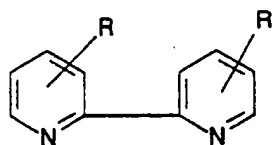
where n is 1 or 2, preferably 2, and in which Ru is ruthenium;

each X independently is selected from Cl, SCN, H₂O, Br, I, CN, -NCO and SeCN; and

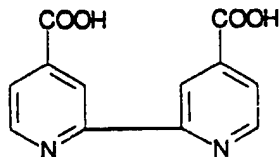
L is a ligand of the formula



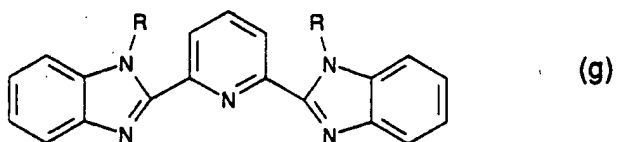
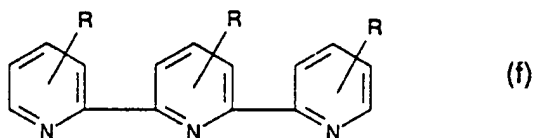
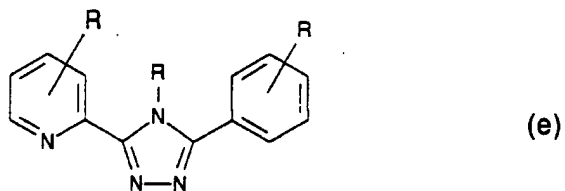
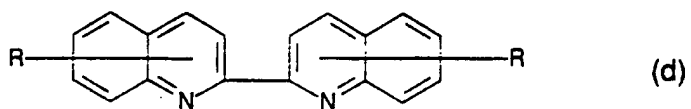
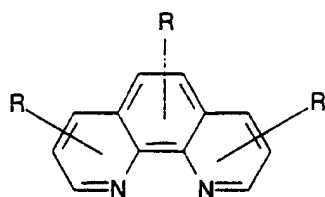
and L₁ is selected from a ligand of formula a) to g)



(a)



(b)

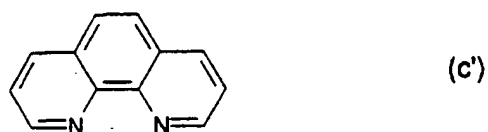
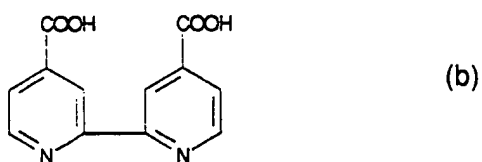
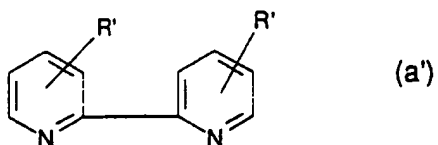


where each R independently is selected from OH, hydrogen, C_{1-20} alkyl, $-OR_a$ or $-N(R_a)_2$ and each R_a independently is hydrogen or C_{1-4} alkyl

Preferred groups of L_1 are those of formula a), b), c) and d).

Preferably X is X' where X' is Cl, CN, -NCO or -SCN.

Preferably L₁ is L₁' where L₁' is selected from a ligand of formula a', b, and c'

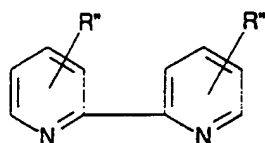


in which R' is OH, hydrogen or C₁₋₂₀alkyl, (more preferably R'' where R'' is hydrogen or C₁₋₂₀alkyl).

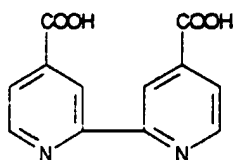
More preferred compounds of formula I are of formula II



in which L'' a group of formula a'' or b



(a'')

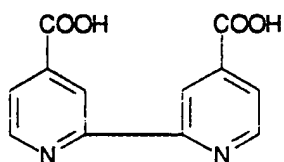


b)

L is as defined above:

X' is selected from Cl, CN -NCO and SCN; and
R'' is C₁₋₂₀alkyl (preferably C₁₋₁₅alkyl) or hydrogen

Most preferably L'' is a ligand of the formula b)



Especially preferred is cis and trans (preferably cis) -dithiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium (II).

Preferably in formulae a, a' and a'', the group R and R' respectively are located in the para position to the N atom in the 4-position.

According to the invention there is provided a photovoltaic cell comprising:

an electrically conductive layer (preferably light transmitting) deposited on a support

(preferably glass plate, a transparent polymer sheet or a metal surface) to which one or more (preferably porous high surface area) titanium dioxide layers have been applied, characterized by applying a compound of formula I defined above (as a photosensitizer) to the TiO_2 layer.

Still further according to the invention, there is provided a photovoltaic cell comprising:

- i) two electrodes, at least one of which is transparent and has a visible light transmittance of at least 60%, the plates being arranged so as to define a receptacle between them, in which receptacle an electrolyte is located, one of the electrodes having a film of titanium dioxide (preferably high surface area) the film being coated with a photosensitizer; and
- ii) means for permitting the passage of an electrical current generated by the cell;

characterized in that the photosensitizer is a compound of formula I defined above.

Preferably a photovoltaic cell according to the invention comprises

- i) an electrically conductive first plate to which a film of titanium dioxide is applied, (the film preferably having a thickness of 0.1-50 microns) and the film being coated with a photosensitizer; and
- ii) a conductive second plate with no TiO_2 film separated from the first plate by a thin layer of electrolyte, whereby the visible light transmittance of at least one of the plates is at least 60%; (preferably also for solar light);

characterized in that the photosensitizer is a compound of formula I defined above.

The second plate (also known as "the counterelectrode") may be coated with a thin layer (preferably up to 10 microns thickness) of an electrocatalyst. The role of the electrocatalyst is to facilitate the transfer of electrons from the counterelectrode to the electrolyte. A further possible modification of the counterelectrode is to make it

reflective to light that has first passed through the electrolyte and the first plate.

Further the outside of the glass plates may be coated with plastics like PS, PMMA or preferably PC to protect the TiO_2 layer, the dyestuff and the electrolyte against UV-light to give long term stability.

Preferably the electrolyte contains a redox system (charge transfer relay). Preferably such systems include iodine/iodide solutions, bromine/bromide solutions, hydroquinone solutions or solutions of transition metal complexes transferring a nonbonding electron. The charge transfer relays present in the electrolyte transport electric charge from one electrode to the other. They act as pure mediators and undergo no chemical alteration during the operation of the cell. It is preferable that the electrolytes in a photovoltaic cell according to the invention, are dissolved in an organic medium so that the dyes applied to the titanium dioxide surface are insoluble therein. This has the advantage that the cell has a long-term stability.

Preferred organic solvents for the electrolyte include but are not limited to water, alcohols and mixtures thereof, non-volatile solvents such as 3-methyl(-2-oxazolidinone (NMO), 1,3-dimethyl-2-imidazolidinone (DMEN), propylene carbonate, ethylene carbonate and methyl pyrrolidinone, mixtures of non-volatile solvents with viscosity reducing solvents such as acetonitrile, ethylacetate or tetrahydrofuran. Additional solvents are dimethylsulfoxide or dichloroethane. Where miscible, mixtures of any of the above may be used.

Preferably the titanium dioxide films have a roughness factor greater than one, the roughness factor being defined as the ratio of true to apparent surface area. More preferably the roughness factor is 10-1000, most preferably 50-200. Preferably the titanium dioxide layers are built up on the surface of the conductive layer using one of two methods. One, the sol-gel method is described in "Stalder and Augustynski, J. Electrochem. Soc. 1979, 126:2007" and in Application Example A. The other, the "colloidal method" is described in Application Examples B and D.

In the sol gel method it is preferable that only the last three, the last two or just the very top layer of the titanium dioxide is doped with a divalent or trivalent metal in an amount of not more than 15% doping by weight. However, the deposition of the pure dopant in form of a very thin top oxide layer can also be advantageous. In the latter cases a blocking layer is formed which impedes leakage current at the semiconductor-electrolyte junction. All of the TiO_2 layers are formed by the sol gel process method described in Application Example A. Preferably the number of TiO_2 layers deposited is 10-11. Preferably the total thickness of the TiO_2 film is from 5 to 50 microns (more preferably 10-20 microns).

The glass or polymer plate which is used for the transparent plate of the cell according to the invention is any transparent glass or polymer onto which a light transmitting electrically conductive layer has been deposited, such that the plate preferably has a visible light transmittance of 60-99%, more preferably 85-95%. Preferably the transparent conductive layer has a surface resistance of less than 10 ohms per square cms, preferably from 1 to 10 ohms per square cm. Preferably the transparent conductive layer used in a photovoltaic cell according to the invention is made of tin dioxide doped with ca. 0.8 atom percent of fluorine and this layer is deposited on a transparent substrate made of low-cost soda lime float glass. This type of conducting glass can be obtained from Asahi Glass Company, Ltd. Tokyo, Japan. under the brand name of TCO glass. The transparent conductive layer can also be made of indium oxide doped with up to 5% tin oxide, deposited on a glass substrate. This is available from Balzers under the brand name of ITO glass.

The photosensitising layer may be produced by applying to the TiO_2 layer a dye according to the invention defined below.

Cis- $(\text{X})_2$ bis(2,2'-bipyridyl-4,4'-dicarboxylate)-ruthenium(II) complexes ($\text{X}=\text{Cl}, \text{Br}, \text{CN}$ and SCN) act as charge transfer sensitizers for nanostructured TiO_2 films (thickness 8-12 μm) of very high internal surface area (roughness factor ca. 1000), prepared by sintering of 15-30 nm-sized colloidal titania particles on a conducting glass support. The

performance of cis-dithiocyanatobis (2,2'-bipyridyl-4,4'-dicarboxylate)-ruthenium(II) is especially good. Nano-structured TiO_2 films coated with a mono layer of 1μ harvest visible light very efficiently, their absorption threshold being around 800 nm. Conversion of incident photons into electric current is nearly quantitative over a large spectral range. These films can be incorporated in a thin layer regenerative solar cell equipped with a light-reflecting counterelectrode. The open circuit voltage can be increased usefully by treating the dye-covered film with 4-tert butylpyridine. The effect of temperature on the power output and long term stability of the dye is also investigated. For the first time, a device based on a simple molecular light absorber attains a conversion efficiency commensurate with that of conventional silicon based photovoltaic cells.

While tris(2,2'-bipyridyl)ruthenium(II) and its homologues have been extensively investigated as redox sensitizers, very little is known about the excited state redox properties of the bis(2,2'-bipyridyl)ruthenium(II) analogues. The reason for this is that the excited state of these compounds is often too short-lived to allow for occurrence of homogeneous bimolecular electron transfer reactions. However, heterogeneous charge transfer processes might still be initiated with such sensitizers since they can take place over a very short time scale. Apart from their chemical stability and ease of interfacial charge exchange with semiconducting solids, it has been found that these complexes have a large visible light harvesting capacity which is superior to that of the widely studied trisbipyridyl Ru(II) analogues, making them useful for use in a solar energy conversion device.

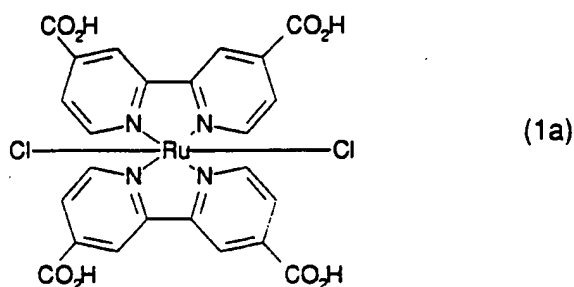
One aspect of the invention relates to Ru(II) complexes having the general formula cis-(X)₂bis (2,2'-bipyridyl-4,4'-dicarboxylate)-ruthenium(II) complexes, where X is Cl, Br, I, CN and SCN. Among these complexes cis-dithiocyanatobis (2,2'-bipyridyl-4,4'-dicarboxylate)-ruthenium(II) displays outstanding properties as a charge transfer sensitizer. Its broad range of visible light absorption and relatively long-lived excited state renders it an attractive sensitizer for homogeneous and heterogeneous redox reactions. In conjunction with the recently developed nanostructured colloidal TiO_2 films and the iodide/triiodide electrolyte in an acetonitrile/3-methyl-2-oxazolidinone solvent

mixture, this complex converts an appreciable amount of AM1.5 solar radiation into electrical energy approaching the performance of polycrystalline silicon photovoltaic cells.

The invention will now be illustrated by the following Examples.

Example 1

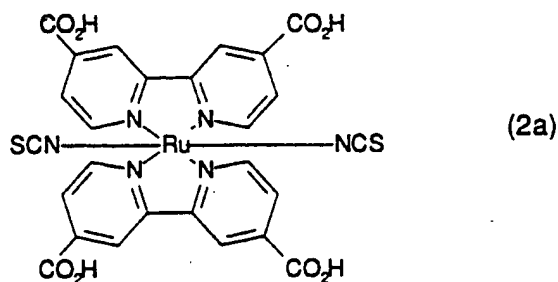
Preparation of Ru-bis(4,4'-COOH-2,2'-bipyridyl)-dichloride dihydrate, a compound of formula 1a



Cis-Ru(II)L₂Cl₂·2H₂O is obtained by refluxing under Ar 60 mg (0.229 mmol) of RuCl₃·3H₂O (Fluka 38-40% Ru) and 113 mg (0.463 mmol) of ligand L=2,2'-bipyridyl-4,4'-dicarboxylic acid (Aldrich) in 20mL of DMF for 8 hours. After cooling, traces of RuL₃ are filtered. Most of the DMF solvent is evaporated under vacuum and cis-Ru(II)L₂Cl₂ is precipitated with acetone. The crystals are filtered off and dried in vacuum. Elemental analysis corresponds to C₂₄H₁₆N₄O₈Cl₂Ru·2H₂O

Example 2

Preparation of cis-dithiocyanato-N-bis(2,2'-bipyridyl-4,4'-di-carboxylic acid) ruthenium(II), dihydrate [RuL₂(NCS)₂]·2H₂O, a compound of formula 2a



283 mg of (0.428mmol) RuL_2Cl_2 are dissolved in 30 ml of DMF, under reduced light. 350mg (4.25mmol) of sodium thiocyanate are separately dissolved in 2ml of water and subsequently added to the above solution. Then the reaction mixture is heated to reflux for 6 hours under a nitrogen atmosphere, while maintaining magnetic stirring. After this time, the reaction mixture is allowed to cool and then the solvent is removed on a rotary evaporator. The resulting solid is dissolved in water and filtered through a sintered glass crucible. The pH of this filtrate is lowered to 2.5 by adding dilute HClO_4 or $\text{CF}_3\text{SO}_3\text{H}$ and placed in a refrigerator over night. After allowing it to reach room temperature, the micro crystalline solid is isolated by suction filtration, washed well with water acidified with HClO_4 to pH3 and acetone-ether mixture (1:10) followed by anhydrous diethylether and air dried for an hour. The yield is 80%. Elemental analysis for $\text{C}_{26}\text{H}_{16}\text{N}_6\text{S}_2\text{O}_8\text{Ru}\cdot 2\text{H}_2\text{O}$ gives (calculated values in brackets): C41.65(42.1); H2.86(2.272); N11.26(11.34).

Further structural characterization of 2a can be carried out by IR spectroscopy using a DA 3.26 (BOMEM Inc., Quebec, Canada) FTIR or a Perkin-Elmer 6811 instrument. The high resolution spectrum exhibits a doublet with peaks at 2126 and 2093 cm^{-1} which is characteristic of the *cis*-configuration of the two thiocyanate ligands. Furthermore, the N-coordination of the thiocyanate group is confirmed by the presence of the $\nu(\text{C}=\text{S})$ resonance at 770 cm^{-1} .

Example 3

- a) Synthesis of $\text{RuCl}_2(\text{DMSO})_4$ where the DMSO = dimethylsulphoxide.

1g of Ruthenium trichloride trihydrate is refluxed in 5ml of dimethylsulphoxide for 1 hour. After this period of time, the addition of acetone gives a yellow precipitate. The yellow complex which separates is filtered off, washed with acetone and diethylether. The yield is about 80%

- b) Synthesis of $\text{RuCl}_2(\text{L})(\text{DMSO})_2$ where L is 4,4'-dimethyl-2,2'-bipyridine.

1 equivalent of $\text{RuCl}_2(\text{DMSO})_4$, prepared above and 1 equivalent of 4,4'-dimethyl-2,2'-bipyridine are refluxed in chloroform for 1 hours. The solution is cooled and the solvent is removed on a rotary evaporator. The resultant solid is dissolved in acetone and filtered. Addition of diethylether to the filtrate gives a yellow precipitate. This is collected on glass frit, washed with ether and vacuum dried (giving about 80% yield).

- c) Synthesis of RuLL_1Cl_2 where L is 4,4'-dimethyl-2,2'-bipyridine and L_1 is 4,4'-carboxy-2,2'-bipyridine (hereinafter the complex of Example 3c).

1 equivalent of $\text{RuCl}_2\text{L}(\text{DMSO})_2$, prepared above and 1 equivalent of 4,4'-dicarboxy-2,2'-bipyridine are placed in dimethylformamide and the mixture is refluxed for 3-4 hours in the dark. After this period, the reaction mixture is filtered through sintered glass crucible. The filtrate is evaporated and the resultant solid is washed with a 1:1 mixture of acetone/ether and then washed with diethylether and vacuum dried.

Example 4

Synthesis of $\text{RuLL}_1(\text{SCN})_2$ where L is 4,4'-dimethyl-2,2'-bipyridine and L_1 is 4,4'-carboxy-2,2'-bipyridine (hereinafter the complex of Example 4):

This is prepared by an analogous procedure to that described in Example 2 from appropriate reactants.

Example 5

- a) Synthesis of $\text{RuCl}_2(\text{L})(\text{DMSO})_2$ where L is 2,2'-bipyridine. This is prepared by an analogous procedure to that described in Example 3b from appropriate reactants
- b) Synthesis of RuLL_1Cl_2 where L is 2,2'-bipyridine and L_1 is 4,4'-carboxy-2,2'-bipyridine. This is prepared by an analogous procedure to that described in 3c

from appropriate reactants.

Example 6

Synthesis of $\text{RuLL}_1(\text{SCN})_2$ where L is 2,2'-bipyridine and L_1 is 4,4'-carboxy-2,2'-bipyridine. This is prepared by an analogous procedure to that described in example 2 from appropriate reactants.

Example 7

- a) Synthesis of $\text{RuCl}_2(\text{L})(\text{DMSO})_2$ where L is 4,4'-di- C_{13} alkyl-2,2'-bipyridine. This is prepared by an analogous procedure to that described in example 3b from appropriate reactants.
- b) Synthesis of RuLL_1Cl_2 where L is 4,4'-di- C_{13} alkyl-2,2'-bipyridine and L_1 is 4,4'-dicarboxy-2,2'-bipyridine. This is prepared by an analogous procedure to that described in example 3c from appropriate reactants

Example 8

Synthesis of $\text{RuLL}_1(\text{NCS})_2$ where L is 4,4'-di- C_{13} alkyl-2,2'-bipyridine and L_1 is 4,4'-dicarboxy-2,2'-bipyridine. This is prepared by an analogous procedure to that described in example 2 from appropriate reactants

Example 9

Cis-Dicyanobis(2,2'-bipyridyl-4,4'-dicarboxylic acid) ruthenium(II)trihydrate is synthesized by dissolving 235 mg (3.6mmol) of KCN in 10ml of H_2O and transferring it into a three-neck flask containing 30ml of DMF. Subsequently, 500mg (0.76 mmol) of $\text{RuL}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ of Example 1 are introduced into the above solution. The reaction mixture is then heated to reflux under nitrogen for 5 hours. During this period, the

initially violet color of the solution changes to orange. After this time, the reaction mixture is allowed to cool and then filtered through a glass frit. The filtrate is evaporated to dryness on a rotary evaporator and the resulting solid is dissolved in H_2O at pH 10. Upon addition of dilute HClO_4 or $\text{CF}_3\text{SO}_3\text{H}$ to the above solution, most of the complex precipitates as a neutral salt at pH 2-3. The orange solid is isolated by suction filtration, washed well with H_2O , ethyl alcohol, followed by anhydrous diethylether and air dried for an hour. The yield is 70%.

Example 10

Synthesis of $[\text{Ru L (PPh}_3)_2(\text{Cl})_2]$ where L is selected from the ligands 4,4-dicarboxy-2,2-bipyridine (the ligand of formula b).

This is prepared by analogous procedure to that described in example 3b from appropriate reactants, using low or high boiling organic solvents. Most preferable solvent is acetone.

Ph=phenyl

Example 11

Synthesis of $[\text{RuLL}_1(\text{Cl})_2]$ where L is selected from the ligand of formula b and L_1 is 4,4-COOH-2,2-bipyridine.

This is prepared by analogous procedure to that described in example 3c from appropriate reactants, using low or high boiling organic solvents. Most preferably solvent is N,N-dimethylformamide.

Example 12

Synthesis of $[\text{RuLL}_1(\text{NCS})_2]$ where L is selected from the ligand of formula b) and L_1 is

4,4 COOH-2,2-bipyridine. This is prepared by an analogous procedure to that described in example 2 from appropriate reactants.

Example 13

a) Synthesis of $[\text{Ru}(\text{CO})_2(\text{Cl})_2]_n$ where n is 2 or 3.

Ruthenium trichloride (1gr) is refluxed with 90% formic acid until the solution changes from green to yellow over 3-4 hours. The solution is then filtered and evaporated on the steam bath to give the bright a yellow product, having yield of 90%.

b) Synthesis of $[\text{Ru L} (\text{CO})_2(\text{Cl})_2]$ where L is selected from the ligand of formula (b). This is prepared by analogous procedure to that described in example 3b using low or high boiling solvents. Most preferable solvent is EtOH or MeOH. When appropriate reactants i.e. the compound of example 13a and the ligand b) are heated at reflux in MeOH for 15 to 60 minutes, the yellow solid precipitates and is isolated as a fine yellow crystals having yield of 90%.

c) Synthesis of $[\text{RuLL}_1(\text{Cl})_2]$ where L and L_1 are 4,4-COOH-2,2-bipyridine. This is prepared by analogous procedure to that described in example 3c from appropriate reactants, i.e. the compound of example 13b and 4,4-COOH-2,2-bipyridine using low or high boiling organic solvents. Most preferable solvent is N,N-dimethylformamide.

Example 14

Synthesis of $[\text{RuLL}_1(\text{NCS})_2]$ where L and L_1 are 4,4-COOH-2,2-bipyridine. This is prepared by an analogous procedure to that described in example 2 from appropriate reactants i.e. the compound of example 13c and NaNCS.

Example 15

Synthesis of $[\text{RuLL}_1\text{Cl}_2]$ where L is 4,4 -COOH-2,2-bipyridine and L_1 is selected from the group of formula (c), where R is hydrogen.

Example 16

Synthesis of $[\text{RuLL}_1\text{Cl}_2]$ where L is 4,4'-COOH-2,2'-bipyridine and L_1 is selected from the group of formula (d), where R is hydrogen.

Example 17

Synthesis of $[\text{RuLL}_1\text{Cl}_2]$ where L is 4,4'-COOH-2,2'-bipyridine and L_1 is selected from the group of formula (e), where R is hydrogen.

These compounds i.e. example 15, 16 and 17 can be prepared by an analogous procedure to that described in example 3c from appropriate reactants.

Example 18

a) Synthesis of $[\text{RuL}_1(\text{Cl})_3]$.

1 equivalent of Ruthenium trichloride and 1 equivalent of L_1 [where L_1 is selected from the ligand of the formula (f) or (g) where R is hydrogen] are refluxed in EtOH for 30 to 60 minutes. After this period, the resulting solid was collected on G4 crucible and washed with EtOH.

b) Synthesis of $[\text{RuLL}_1\text{Cl}]$ where L is 4,4'-COOH-2,2'-bipyridine and L_1 is selected from the group of formula (f) where R is hydrogen. This is prepared by refluxing 1 equivalent of $[\text{RuL}_1(\text{Cl})_3]$ and 1 equivalent of L in DMF for 3 to 5 hours. After allowing to room temperature, the solvent DMF is evaporated and the resulted solid is dissolved in water. The pH of this solution is adjusted to 2.5 by diluted HClO_4 , which give a dense precipitate. This precipitate is collected on crucible and washed with water acidified with HClO_4 to pH 3 and acetone-ether mixture followed by anhydrous diethyl ether. The product was air dried for 2 hours.

Example 19

Synthesis of $[\text{RuLL}_1\text{Cl}]$ where L is 4,4'-COOH-2,2'-bipyridine and L_1 is selected from the group of formula (g) where R is hydrogen. This is prepared by an analogous procedure to that described in example 18b from appropriate reactants i.e. the compound of formula 18a and 4,4'-COOH-2,2'-bipyridine.

Application Example A

A photovoltaic device shown in Figure 1 and based on the sensitization of an aluminum-doped titanium dioxide film supported on conducting glass is fabricated as follows:

A stock solution of organic titanium dioxide precursor is prepared by dissolving 21 mmol of freshly distilled TiCl_4 in 10mL of absolute ethanol. TiCl_4 in ethanol solution gives titanium alkoxide spontaneously which, on hydrolysis, gives TiO_2 . The stock solution is then diluted with further absolute ethanol to give two solutions (solution A and solution B having) titanium contents of 25mg/ml (solution A) and 50 mg/ml (solution B). A third solution (C) is prepared from solution B by addition of AlCl_3 to yield an aluminium content of 1.25 mg/ml. A conducting glass sheet provided by Asahi Inc. Japan, surface area 10 cm^2 and having a visible light transmittance of at least 85% and a surface resistance smaller than 10 ohms per square cm is used as support for a deposited TiO_2 layer. Prior to use, the glass is cleaned with alcohol. A droplet of solution A is spread over the surface of the conducting glass to produce a thin coating. Subsequently the layer is hydrolyzed at 28°C for 30 minutes in a special chamber, where the humidity is kept at 48% of the equilibrium saturation pressure of water. Thereafter, the electrode is heated in air in a tubular oven kept at 450°C , preheating it in the entrance of the oven for 5 minutes followed by 15 minutes of heating in the interior. Three more layers are produced in the same way. Subsequently, 5 thicker layers are deposited by using solution B. The same procedure as for the first layers is applied. Finally, solution C is used to deposit the last two layers containing the aluminum dopant. The heating of the last layer in the tubular oven is extended from 15 to 30 minutes. The total thickness of the titanium dioxide film is between 10 and 20 microns.

Prior to deposition of the dye, the film is subjected to a sintering treatment in highly purified 99.997% argon. A horizontal tubular oven composed of quartz tubes with suitable joints is employed. After insertion of the glass sheet with the TiO_2 film, the tube is twice evacuated and purged with argon. The glass sheet is then heated under argon

flux at a flow rate of 2,5L/h and a temperature gradient of 500°C/h up to 550°C at which temperature it maintained for 35 minutes. This treatment produces anatase films with a surface roughness factor of 80-200.

After cooling under a continuous argon flow, the glass sheet is immediately transferred to an alcoholic solution (or alcohol/dimethylsulfoxide mixture) of a chromophore. The chromophore employed is the complex of Example 2. Its concentration in absolute ethanol is 5×10^{-4} M. Prolonged exposure of the film to the open air prior to dye adsorption is avoided in order to prevent hydroxylation of the TiO_2 surface as the presence of hydroxyl groups at the electrode surface interferes with dye uptake. The adsorption of chromophore from the ethanolic solution is allowed to continue for 30 minutes after which time the glass sheet is withdrawn and washed briefly with absolute ethanol. The TiO_2 layer on the sheet assumed a deep red colour owing to the chromophore coating.

The photocurrent action spectrum obtained with such a film using a conventional three electrode electrochemical cell containing an ethanolic solution of 0.5M LiI and 3×10^{-3} M iodine is shown in the attached figure together with the AM 1 spectral distribution of solar light emission. The incident monochromatic photon to current conversion efficiency (IPCE) is plotted as a function of the excitation wavelength. This was derived from the equation:

$$(1) \quad \text{IPCE}(\%) = \frac{[(1.24 \times 10^3) \times \text{photocurrent density } (\mu\text{A}/\text{cm}^2)]}{[\text{wavelength (nm)} \times \text{photon flux (W}/\text{m}^2)]}$$

From the overlap of the photocurrent action spectrum with solar emission the overall efficiency for the conversion of solar light to electricity η is calculated from the formula

$$(2) \quad \eta = 12 \times \text{OCV} \times \text{FF}(\%)$$

where OCV is the open circuit voltage and FF is the fill factor of the photovoltaic cell.

For experimental verification of equation 2, a photovoltaic cell, shown in the drawing attached, is constructed, using the dye of Example 1 (4)-loaded TiO_2 (5) film supported on a conducting glass (the working electrode) comprising a transparent conductive tin dioxide layer (6) and a glass substrate (7) as a photoanode. The cell has a sandwich-like configuration, the working electrode (4-7) being separated from the counter electrode (1,2) by a thin layer of electrolyte (3) having a thickness of ca. 20 microns. The electrolyte used is an ethanolic solution of 0.5M LiI and $3 \times 10^{-3}\text{M}$ iodine. The electrolyte (3) is contained in a small cylindrical reservoir (not shown) attached to the side of the cell from where capillary forces attract it to the inter-electrode space. The counter-electrode comprises the conductive tin dioxide layer (2) deposited on a glass substrate (1) made also of Asahi conducting glass and is placed directly on top of the working electrode. A monomolecular transparent layer of platinum is deposited on to the conducting glass of the counter electrode (1,2) by electroplating from an aqueous hexachloroplatinate solution. The role of the platinum is to enhance the electrochemical reduction of iodine at the counter electrode. The transparent nature of the counterelectrode is an advantage for photovoltaic applications since it allows the harvesting of light from both the forward and the backward direction. Experiments are carried out with a high pressure Xenon lamp equipped with appropriate filters to simulate AM1 solar radiation. The intensity of the light is varied between 50 and 600 Watts per square meter and the open circuit voltage is 660 and 800mV, respectively at these two voltages. The fill factor defined as the maximum electric power output of the cell divided by the product of open circuit voltage and short circuit current is between 0.7 and 0.75V. A single crystal silicon cell gave an open voltage of 550mV at $600\text{W}/\text{m}^2$ incident light intensity which dropped to below 300mV at $50\text{W}/\text{m}^2$. This clearly shows that the cell of the present invention has a higher open circuit voltage than the silicon solar cell and that the open circuit voltage is less dependent on light intensity than that of the silicon cell. This constitutes a significant advantage for the use of such a cell in indirect sunlight or cloudy weather conditions. The fill factor of the silicon cell is comparable to that of the example. The overall solar light to electricity conversion

efficiency of the cell of the example is between 5 and 6% in agreement with predictions of equation 2.

Application Example B

A transparent TiO_2 film from colloidal titanium dioxide particles which are deposited on a conducting glass support and sintered to yield a coherent highly porous semiconducting film that is transparent and can be used instead of the TiO_2 layer film in Application Example A.

Colloidal titanium oxide particle of approximately 10nm are prepared by hydrolysis of titanium isopropoxide as follows:

125 ml of titanium isopropoxide is added to a solution of 0.1M nitric acid in 750ml of water whilst stirring. A precipitate of amorphous titanium dioxide is formed under these conditions. This is heated to 80°C for approximately 8 hours, stirring vigorously, resulting in peptisation of the precipitate and formation of a clear solution of colloidal anatase. The anatase structure of the titanium dioxide particles is established by Raman spectroscopy. The sol is concentrated by evaporation of the solvent in vacuum at room temperature until a viscous liquid is obtained containing the colloidal particles. At this stage the nonionic surfactant TRITON X-100 (40% weight of TiO_2) is added to reduce cracking of the film when applied to a substrate.

The titanium dioxide films are formed by spin coating the concentrated sol on to a conducting glass substrate. Usually it is sufficient to apply 6 to 10 layers in order to obtain semiconductor membranes of sufficient surface area to give excellent visible light harvesting efficiencies after deposition of a monolayer of the sensitizer.

Low resolution electron microscopy confirms the presence of the three layer structure, the lowest being the glass support followed by the 0.5 micron thick fluorine-doped SnO_2 and the 2.7 micron thick titanium dioxide layer. High resolution electron microscopy

reveals the TiO_2 film to be composed of a three dimensional network of interconnected particles having an average size of approximately 16nm. Apparently, significant particle growth occurs during sintering.

The transparent TiO_2 films are tested in conjunction with a sensitizer, the dye of Example 2 regenerative cell for the generation of electricity from visible light. The results can be represented where the photocurrent under simulated sunlight (intensity ca 30W/m^2) is plotted as a function of cell voltage.

Application Example C

A sheet of conducting glass (ASAHI) area resistance ca 10 Ohm/square cm having a size of $2 \times 9.6\text{ cm}^2$ is coated with a colloidal titanium dioxide film according to the procedure of Example B. A total of 7 layers of TiO_2 colloid are deposited successively by spin coating and the film is subjected each time to calcination at 500°C for 30 minutes. 30% (w/w) of TRITON X 405 surfactant is added in order to avoid cracking of the film.

The final thickness of the titanium dioxide film is 5 microns as determined from the optical interference pattern. It is important to note that the conducting glass sheet after deposition of the TiO_2 remains clear and transparent to visible and near infrared light. The transmission spectrum recorded on a conventional spectrophotometer shows that a fraction of more than 60% of the visible light in the wavelength region between 400 and 900 nm is transmitted through the film. A UV/visible absorption spectrum of the electrode can be obtained. It exhibits a flat feature in the visible due to light absorption and scattering by the conducting glass and the 5 nm thick TiO_2 film. The steeply rising part of the absorption below 400 nm is due to the band gap absorption of the TiO_2 .

Immediately before coating with dyestuff, the film is fired for 1 hour at 500°C . The coating of TiO_2 with dyestuff is performed by immersing the glass sheet for 16 hours in an ethanolic (or alcohol/dimethylsulfoxide mixture) solution containing the complex of

Example 2. After coating, the glass sheet displays an intensive dark red coloration. The optical absorption spectrum measured with a conventional UV/visible spectrophotometer shows the absorbance in the vicinity of 500nm to exceed the value of 2, indicating that in this wavelength range more than 99% of the photons are absorbed by the dyestuff deposited on to the titanium dioxide film. It is important to note that, due to the high concentration of dyestuff, the porous film is capable of harvesting photons over a very broad spectral range extending from 450 to 850 nm.

After dye deposition, the glass sheet is cut into two parts each having a size of ca 9 cm². These sheets serve as working electrodes (photo-anodes) in the module whose assembly is described further below.

Transparent counterelectrodes are made of the same type of ASAHI conducting glass as the working electrodes. The counterelectrode is not coated with TiO₂. Instead, the equivalent of 10 monolayers of Pt is electrochemically deposited on to conducting glass. The transparent nature of the counterelectrode is not affected by the deposition of the Pt its transmission in the visible and near infrared remaining greater than 60%. The Pt acts as an electrocatalyst, enhancing the rate of reduction of the electron transfer mediator, i.e. triiodide, at the counterelectrode. Two ca. 1mm deep and 1.5mm wide and 20mm long indentations are engraved into the surface of the counterelectrode close to the edges of the glass sheets. These serve as a reservoir for the electrolyte.

The counter electrode is placed directly on top of the working electrode to yield a sandwich-type configuration. After filling the reservoirs with electrolyte, the cell was sealed with epoxy resin. The wetting of the space between the two electrodes by the electrolyte occurs spontaneously by capillary action. The electrolyte is a solution of 0.5M tetrapropyl ammonium iodide and 0.02M iodine in ethanol.

Two cells are fabricated in this way, each having a surface area of ca 9cm². Subsequently they are connected in series by electrically contacting the photoanode of one cell to the cathode of the second cell. In this way a module is constructed,

having a total surface area of 18cm².

Application Example D

Nanostructured TiO₂ films are prepared by spreading a viscous dispersion of colloidal TiO₂ particles on a conducting glass support (Asahi TCO glass, fluorine-doped SnO₂ overlayer, transmission ca 85% in the visible, sheet resistance 8 Ohm/square cm) and subsequent heating under air for 30 min at 30-450°C (preferably 450°C). Two methods of preparation of colloidal TiO₂ dispersions are employed.

- a) The procedure of Application Example C is repeated except that autoclaving is performed at 230 to 240°C instead of 500°C. After spreading the colloid on the conducting glass support and calcining, a few monolayers of TiO₂ are electrodeposited onto the colloidal TiO₂ film from an aqueous Ti(III) solution followed by renewed annealing at 450°C. This treatment is found to improve significantly the short circuit photocurrent as well as the open circuit voltage of the solar cell. Low resolution electron microscopy confirms the presence of a three-layer structure, the lowest being the glass support followed by the 0.7 µm thick fluorine-doped SnO₂ and the 10µm thick colloidal TiO₂ film. High resolution electro microscopy reveals the TiO₂ film to be composed of a three-dimensional network of interconnected particles having an average size of approximately 15 nm.

- b) The second method for preparation of nanostructured films (Method B) employed commercial TiO_2 (P25, Degussa AG, Germany, a mixture of ca 30% rutile and 70% anatase). This is produced by flame hydrolysis of TiCl_4 and consists of weakly aggregated particles. The BET surface area is $55 \text{ m}^2/\text{g}$, corresponding to a mean particle size of about 25 nm. In order to break the aggregates into separate particles, the powder (12g) is ground in a porcelain mortar with a small amount of water (4ml), containing acetylacetone (0.4ml) to prevent reaggregation of the particles. Other stabilizers such as acids, bases or TiO_2 chelating agents are found to be suitable as well. After the powder has been dispersed by the high shear forces in the viscous paste it is diluted by slow addition of water (16ml) under continued grinding. Finally, a detergent (0.2 ml Triton®X-100) is added to facilitate the spreading of the colloid on the substrate. The conducting TCO glass is covered on two parallel edges with adhesive tape ($\sim 40 \mu\text{m}$ thick) to control the thickness of the TiO_2 film and to provide noncoated area for electrical contact. The colloid ($5 \mu\text{l}/\text{cm}^2$) is applied to one of the free edges of the conducting glass and distributed with a glass rod sliding over the tape covered edges. After air drying, the electrode is fired for 30 minutes at $30\text{--}550^\circ\text{C}$ (preferably $450\text{--}550^\circ\text{C}$) in air. The resulting film thickness is $12 \mu\text{m}$ but can be varied by changing the colloid concentration or the adhesive tape thickness.

The performance of the film, as sensitized photoanode, is improved by further deposition of TiO_2 from aqueous TiCl_4 solution. A 2 M TiCl_4 stock solution is prepared at 0°C to prevent precipitation of TiO_2 due to the highly exothermic hydrolysis reaction. This stock solution is freshly diluted with water to 0.2M TiCl_4 and applied onto the electrode ($50 \mu\text{l}/\text{cm}^2$). After standing overnight at room temperature in a closed chamber, the electrode is washed with distilled water. Immediately before dipping into the dye solution it is fired again for 30 minutes at $30\text{--}550^\circ\text{C}$ (preferably $450\text{--}550^\circ\text{C}$) in air. Similarly to the electro-deposition from aqueous Ti(III) solution, this procedure results in the deposition of nano-sized TiO_2 particles on the TiO_2 film further increasing its active surface area. Furthermore, this treatment as well as the anodic deposition of TiO_2 from Ti(III) solution described above appears to lead to deposits having a very low

impurity content. This is corroborated by the fact that the treatment becomes ineffective if the TiCl_4 solution is evaporated before firing instead of being washed off. Impurities in the TiCl_4 , such as Fe^{3+} , are not deposited by hydrolysis from the acidic TiCl_4 solution due to the higher solubility of iron oxide compared to TiO_2 . By contrast, the evaporation of the TiCl_4 solution results in the deposition of impurities. The P25 powder contains up to 100 ppm Fe_2O_3 , which is known to interfere with electro-injection of the excited dye. The TiCl_4 treatment covers this rather impure core with a thin layer of highly pure TiO_2 improving the injection efficiency and the blocking character of the semi-conductor-electrolyte junction.

Coating of the TiO_2 surface with dyestuff is carried out by soaking the film for ca 3h in a 3×10^{-4} M solution of the ruthenium complex from Example 1 in dry ethanol (or alcohol/dimethylsulfoxide mixture). The dye coating is done immediately after the high temperature annealing in order to avoid rehydroxylation of the TiO_2 surface or capillary condensation of water vapor from ambient air inside the nanopores of the film. The presence of water in the pores decreases the injection efficiency of the dye. The electrode is dipped into the dye solution while it is still hot, i.e. its temperature is ca 80°C . After completion of the dye adsorption, the electrode is withdrawn from the solution under a stream of dry air or argon. It is stored in dry ethanol or immediately wetted with the Li/LiI_3 acetonitrile redox electrolyte for testing. The amount of adsorbed dye is determined by desorbing the dye from the TiO_2 surface into a solution of 10^{-4} NaOH in ethanol (or alcohol/dimethylsulfoxide mixture) and measuring its adsorption spectrum.

A BAS-100 electrochemical analyzer (Bioanalytical Systems, USA) is used to perform cyclic voltammetry in electrochemical cells of volumes of 5 to 20 ml. A three-electrode cell is made up of a glassy carbon or Pt disc (3mm diameter embedded in Teflon) working electrode and a platinum wire counter electrode. The reference electrode consists of calomel in contact with 0.1 LiCl in methanol. It is separated from the working electrode compartment by bridge containing the same electrolyte as the test solution, i.e. 0.1M n-tetrabutylammonium perchlorate in acetonitrile or ethanol. All potentials

indicated refer to the aqueous SCE electrode.

Photo-electrochemical experiments are employed a similar cell equipped with a flat pyrex window. Alternatively, the dye sensitized TiO_2 film is incorporated into a thin layer sandwich type solar cell. A light reflecting counterelectrode is employed consisting of a conducting glass support onto which a $2\mu\text{m}$ thick Pt mirror had been deposited by sputtering. The counterelectrode is placed directly on top of the dye coated transparent TiO_2 film supported by the conducting glass sheet. Both electrodes are clamped tightly together. A thin layer of electrolyte is attracted into the inter-electrode space by capillary forces. The dyed coated TiO_2 film is illuminated through the conducting glass support. The conversion efficiencies reported are overall yields which are uncorrected for losses due to light absorption and reflection by the conducting glass support. An Oriel 450W Xe lamp served as a light source in conjunction with a polycarbonate filter to remove ultraviolet radiation and a Schott a 113 interference filter to mimic AM 1.5-type solar emission.

The emission spectra are measured on a Spex Fluorolog II equipped with a 450 W Xenon light source. The measured excitation and emission spectra are routinely corrected for the wavelength-dependent features using correction factors generated by a National Bureau of Standards 150W halogen lamp. The emission detector is a Hamamatsu R2658 photomultiplier which extends the corrected emission measurement over a region from 250 to 1000 nm. All solutions are prepared by dissolving the appropriate amount of complex in the desired solvent to give typically a $2 \times 10^{-5}\text{M}$ solution. The solutions are degassed by freeze, pump and thaw methods. Low temperature measurements are carried out in an Oxford Instruments cryostat.

The emission lifetimes are measured by exciting the sample with active modelocked Nd YAG laser pulse, using the frequency doubled line at 532 nm. The emission decay is followed on a Tektronix DSA 602A Digitizing Signal Analyzer. The digitized xy data is subsequently analyzed and fitted to an exponential model. Sample concentrations were typically $1 \times 10^{-4}\text{M}$. Optical densities are taken from spectra recorded on a Cary 5

spectrophotometer.

Application Example E

A photovoltaic device shown in Figure 1 based on the sensitization of a transparent TiO_2 film made from colloidal titanium dioxide particles which are deposited on a conducting glass support and sintered to yield a coherent highly porous semiconducting film.

Colloidal titanium oxide particles of approximately 8 nm are prepared by hydrolysis of titanium isopropoxide as follows:

125ml titanium isopropoxide is added to a solution of 0.1 M nitric acid in 750ml water while stirring. A precipitate of amorphous titanium dioxide is formed under these conditions. This is heated to 80°C for approximately 8 hours, stirring vigorously, resulting in peptisation of the precipitate and formation of a clear solution of colloidal anatase. The propanol formed by the hydrolysis is allowed to evaporate during the heating. The colloidal solution is then autoclaved at 230 to 240°C, in a pressure vessel of titanium metal or teflon for 2 to 20 hours, preferably 16 hours. The resultant sol, containing some precipitate is stirred or shaken to resuspend the precipitate. The resulting sol, minus any precipitate that will not resuspend, is concentrated by evaporation of the solvent in vacuum at room temperature until a viscous liquid is obtained containing the colloidal particles. A typical concentration at this point is 200g/L. At this stage a polyethylene oxide polymer, for example Union Carbide Carbowax 20M or Triton X-405 can be added to increase the thickness of the layer that be deposited without cracks. The polymer is added in amount of 30 to 50, preferably 40, weight percent TiO_2 .

The electrodes for sensitization are formed from the colloidal solution as follows:

A suitable substrate, for example a 3 x 6 cm piece of conductive tin oxide coated glass, for example from Asahi Corp. (but also titanium metal or any flat conductive surface),

is placed with the conductive surface up and with suitable spacers, for example 50 to 100 micron, preferably 80 micron thick plastic tape, placed along each edge. A suitable amount of the sol, for example 150 microliters of sol with 200 g/L TiO_2 and 40% Carbowax 20M for the above substrate, is pipetted along one end of the substrate. The sol is spread across the substrate by drawing with a flat edged piece of glass whose ends ride along the spacers. Thus the spacers, the viscosity of the sol, and the concentration of the sol control the amount of TiO_2 deposited. The as spread film is allowed to dry in room air till visibly dry and preferable and additional 20 minutes. After drying the electrode is fired at 400 to 500°C, preferably 450, for a minimum of 20 minutes. In the case of sols autoclaved below 170°C the spacers less than 40 micron must be used and the process must be repeated twice to achieve an 8 to 10 micron thick TiO_2 film.

Electrodes of up to 10 cm by 10 cm have been fabricated by this method. The sol can also be applied to substrates by spin coating and dip coating.

The electrode can then be cut to the size desired by normal glass cutting techniques. Immediately before applying the sensitizer the electrode is fired again at 450 to 550, preferably 500°C for 2 to 12, preferably 6 hours. For some solvent and dye combinations the surface of the electrode is improved (with respect to electron injection) by firing the electrode 5 to 10, preferably 7 times at 500°C for 2 to 6 hours with either 10 hours in air or soaking up to 1 hour in water, 0.5M nitric acid or 0.5M HCl, between each firing. The acid solutions are saturated with dissolved TiO_2 before use. After the last firing, immediately after cooling, the electrode is placed in the sensitizer solution. Preferably an ethanolic (or alcohol/dimethylsulfoxide mixture) solution containing the complex of Example 1 is made up. Depending on the sensitizer between 4 and 24 hours are required for the electrode to gain full color. Full color can be estimated by eye or by taking visible light transmittance spectra of the dye at various time.

After removal from the dye solution, the electrode is made into a photovoltaic cell as follows:

Transparent counterelectrodes are made of the same type of ASAHI conducting glass as the working electrodes. The counterelectrode is not coated with TiO_2 . Instead the equivalent of 10 monolayers of Pt is electrochemically deposited onto conducting glass. The transparent nature of the counterelectrode is not affected by the deposition of the Pt, its transmissions is visible and near infrared remains greater than 60%. The Pt acts as an electrocatalyst enhancing the rate of reduction of the electron transfer mediator, i.e. triiodide, at the counterelectrode. Alternatively, a thin titanium sheet, which may be porous coated as above with Pt, may be used as a counter electrode. In the case of a porous sheet, another sheet of impervious material is required behind the counter electrode, such as plastic, glass or metal.

A reservoir is provided for the electrolyte by engraving two ca 1mm deep and 1.5mm wide and 20mm long clefts into the surface of the counterelectrode close to the edges of the glass sheet. The reservoir can also be added external to the glass sheets or be behind the counter electrode in the case of porous counter electrode.

The counterelectrode is placed directly on top of the working electrode to yield a sandwich type configuration. The reservoirs are filled with electrolyte solution, selected from the list above but preferably 85% by weight ethylene carbonate, 15% propylene carbonate 0.5M potassium iodide and 40mM iodine. An amount of LiI or tetraalkylammonium iodide can be present (preferably 20mM) depending on the voltage desired. The cell is sealed around the edge with a sealant compatible with the solvent chosen and bonded closed with an adhesive. The sealant and the adhesive may be the same material for example silicon adhesive in the case of the alcohol solvents, or for example, polyethylene and epoxy resin (or mechanical closure) in the case of ethylene carbonate. The wetting of the space between the two electrodes by the electrolyte injected into the reservoirs occurs spontaneously by capillary action.

Application Examples A to E can be repeated using instead to the compound of Example 2, the same amount of the 4,4-dicarboxy- or 4,4-dialkyl-bipyridyl ruthenium dyes of Examples 1 and 3 to 19.

Claims:

1. A compound of formula I



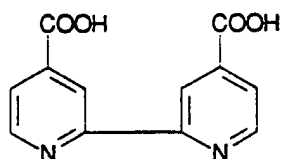
where n is 1 or 2, preferably 2, and in which Ru is ruthenium;

in which Ru is ruthenium;

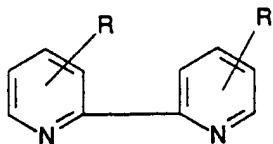
each X independently is selected from Cl, SCN, H₂O, Br, I, CN, -NCO and SeCN;

and

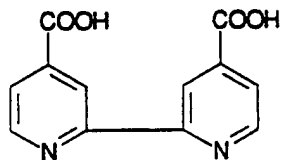
L is a ligand of the formula



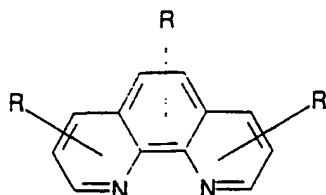
and L₁ is selected from a ligand of formula a) to g)



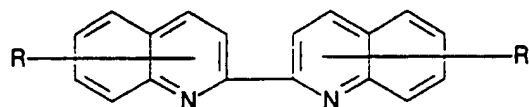
(a)



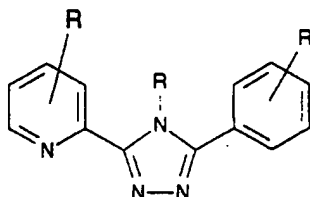
(b)



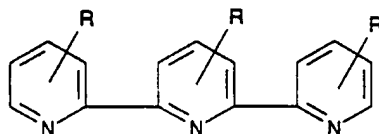
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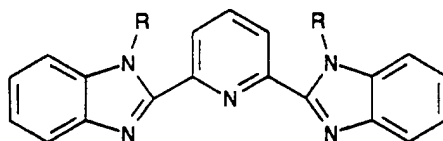
(d)



(e)



(f)

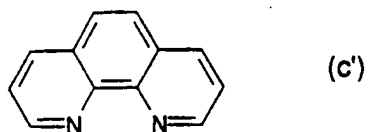
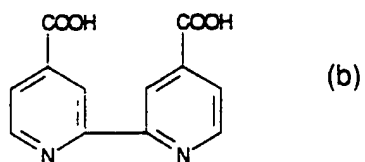
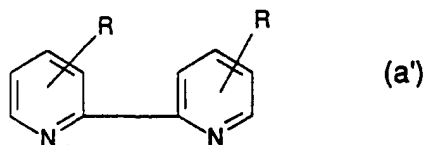


(g)

where each R independently is selected from OH, hydrogen, C_{1-20} alkyl, $-OR_a$ or $-N(R_a)_2$ and each R_a independently is hydrogen or C_{1-4} alkyl

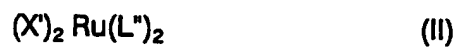
2. A compound according to claim 1 in which X is X' where X' is -Cl, CN, -NCO or -SCN.

3. A compound according to claim 1 or 2 in which L_1 is L_1' where L_1' is selected from a ligand of formula a', b, and c'

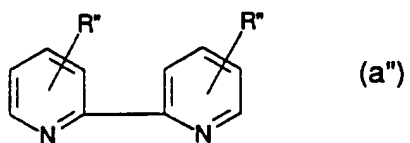


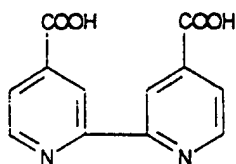
in which R' is OH, hydrogen or C_{1-20} alkyl,

4. A compound of formula II



in which L'' is a group of formula a'' or b





b)

and X' is selected from Cl, NCO, CN and SCN; and

R" is hydrogen or C₁₋₂₀alkyl.

5. Cis or trans -dithiocyanato-bis (2,2'-bipyridyl-4,4'-dicarboxylate ruthenium (II)).
6. Cis-dithiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium (II).
7. A bipyridyl-ruthenium II complex substantially as herein described with reference to any one of Examples 1 to 13.
8. A photovoltaic cell comprising an electrically conductive layer deposited on a support to which one or more titanium dioxide layers have been applied;

characterized by applying a compound of formula I defined above (as a photosensitizer) to the TiO₂ layer.
9. A photovoltaic cell comprising
 - i) two electrodes, at least one of which is transparent and has a visible light transmittance of at least 60%, the plates being arranged so as to define a receptacle between them, in which receptacle an electrolyte is located, one of the electrodes having a film of titanium dioxide the film being coated with a photosensitizer; and
 - ii) means for permitting the passage of an electrical current generated by the cell.

characterized in that the photosensitizer is a compound according to any one of claims 1 to 7.

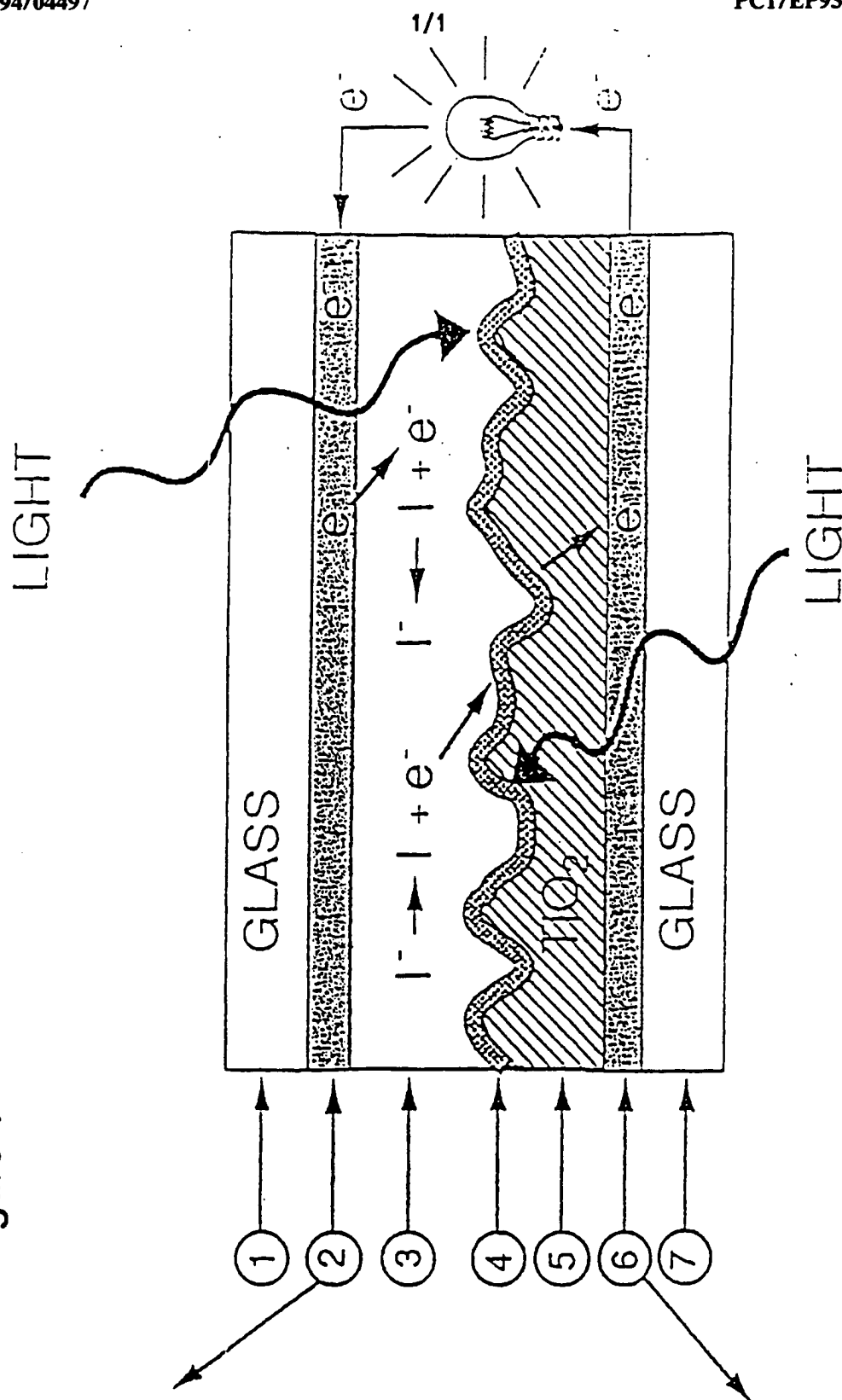
10. A photovoltaic cell comprising

- i) an electrically conductive first plate to which a film of TiO_2 is applied, and the film being coated with a photosensitizer; and
- ii) a conductive second plate with no TiO_2 film separated from the first plate by a thin layer of electrolyte, whereby the visible light transmittance of at least one of the plates is at least 60%;

characterized in that the photosensitizer is a compound according to any one of claims 1 to 7.

11. A photovoltaic cell substantially as herein described with reference to the Application Examples.

Figure 1



INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 93/02221

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC IPC ^S : C 07 D 213/22, C 07 D 215/00, C 07 D 401/04, C 07 D 471/04, C 09 B 57/10, H 01 L 31/04		
II. FIELDS SEARCHED		
Minimum Documentation Searched †		
Classification System	Classification Symbols	
IPC ^S	C 07 D, C 09 B 57/00, H 01 L 31/00	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT*		
Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages ‡	Relevant to Claim No. ††
A	CHEMICAL ABSTRACTS, vol. 90, no. 4, 22 January 1979 (Columbus, Ohio, USA); GAINES, G.L., Jr. et al. "Monolayer films of surfac- tant ester derivatives of tris(2,2'-bipyridine) ruthenium(II)2+", page 384, column 1, abstract no. 29446u, & J. Am. Chem. Soc., 1978, 100(21), 6549-59, (Eng.). --	1-7
A	CHEMICAL ABSTRACTS, vol. 87, no. 16, 17 October 1977 (Columbus, Ohio, USA); SPRINTSCHNIK, GERHARD et al. "Photochemical reactions in organized monolayer assemblies.6.Preparation and photochemical activity of surfactant ruthenium(II)	1-7
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: ††</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>† later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search 19 November 1993	Date of Mailing of this International Search Report 17. 12. 93	
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer SCHARF e.h.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, * with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	complexes in monolayer assemblies and at watersolid interfaces" page 522, column 1, abstract no. 125308 j, & J. Am. Chem. Soc., 1977, 99(15), 4947-54, (Eng.). --	1-7
	CHEMICAL ABSTRACTS, vol. 95, no. 10, 07 September 1981 (Columbus, Ohio, USA), GHOSH, PUSHPITO K. et al. "Electroactive coatings of tris(bipyridyl)- and tris(o-phenantroline)-ruthenium (II) attached to electrodes via hydrosilylation or electropolymerization of vinyl derivatives" page 479, column 1, abstract no. 88183g, & J. Electrochem. Soc., 1981, 128(6), 1281-7 (Eng.). --	
A	US, A, 4 125 414 (TANG et al.) 14 November 1978 (14.11.78), claim 1. --	8-11
A	US, A, 4 127 738 (GHOSH et al.) 28 November 1978 (18.11.78), claim 1. -----	8-11

ANHANG

zum internationalen Recherchen-
bericht über die internationale
Patentanmeldung Nr.

ANNEX

to the International Search
Report to the International Patent
Application No.

ANNEXE

au rapport de recherche inter-
national relatif à la demande de brevet
international n°

PCT/EP 93/02221 SAE 78247

In diesem Anhang sind die Mitglieder
der Patentfamilien der in obenge-
nannten internationalen Recherchenbericht
angeführten Patentdokumente angegeben.
Diese Angaben dienen nur zur Unter-
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This Annex lists the patent family
members relating to the patent documents
cited in the above-mentioned inter-
national search report. The Office is
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La présente annexe indique les
membres de la famille de brevets
relatifs aux documents de brevets cités
dans le rapport de recherche inter-
national visée ci-dessus. Les renseigne-
ments fournis sont donnés à titre indica-
tif et n'engagent pas la responsabilité
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Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche		Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
JS A	4125414	14-11-78	AU A1 38544/78	07-02-80
			AU B2 520193	21-01-82
			CA A1 1086410	23-09-80
			DE C0 2861434	04-02-82
			EP A1 830	21-02-79
			EP B1 830	09-12-81
			JP A2 54027387	01-03-79
JS A	4127738	28-11-78	AU A1 12522/76	06-10-77
			GB A 1535367	13-12-78
			IT A 1058715	10-05-82
			JP A2 51122389	26-10-76